PATENT ABSTRACTS OF JAPAN

(11)Publication number:

06-088025

(43)Date of publication of application: 29.03.1994

(51)Int.CI.

C08L 83/04 C08K 5/54 C09D183/04 C10M107/50 // C10N 50:02

(21)Application number : 04-264286

(71)Applicant: TOSHIBA SILICONE CO LTD

(22)Date of filing:

07.09.1992

(72)Inventor: HORIE YUTAKA

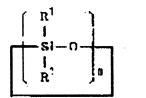
KUWABARA MICHI

(54) DILUENT FOR SILICONE COATING MATERIAL

(57) Abstract:

PURPOSE: To obtain a diluent for silicone coating material excellent in the effect of imparting slipperiness to a coated surface and uniform applicability by incorporating a low-molecular-weight siloxane selected from the group consisting of a specified cyclic siloxane and a specified acyclic siloxane.

CONSTITUTION: At least one low-molecular-weight siloxane selected from the group consisting of a cyclic siloxane of formula I (wherein R1 is H or a monovalent hydrocarbon group; and m is 3-8) and an acyclic siloxane of formula II (wherein R1 is as defined above; and n is 1-6) is incorporated to obtain the diluent. This diluent can give a silicone coating material which can form a cured film excellent in slipperiness and the



$$R^{1} \stackrel{R^{1}}{\stackrel{i}{\rightarrow}} S \stackrel{R}{\longrightarrow} O \stackrel{R^{1}}{\stackrel{i}{\rightarrow}} O \stackrel{R^{1}}{\stackrel{i}{\rightarrow}} R^{1}$$

evenness of film thickness and substantially free from nonuniformity of drying and cissing. This diluent scarcely affects the global environments. When the skin is coated with a silicone coating material containing this diluent, the formed coating film is effective in alleviating a pain during sticking a metallic hypodermic needle in the skin and to reduce the resistance of cutting the skin with a cutter, a surgical knife or scissors to allow good cut with slight force.

LEGAL STATUS

[Date of request for examination]

06.03.1997

[Date of sending the examiner's decision of

13.07.1999

rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or

application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's

decision of rejection]

[Date of requesting appeal against examiner's

decision of rejection]

[Date of extinction of right]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[Industrial Application] This invention relates to the diluent for silicone coating agents which gives the silicone coating agent excellent in the slipping nature grant effectiveness and homogeneity spreading nature on the front face of spreading.

[0002]

[Description of the Prior Art] The organic silicone content polymer is widely used as a silicone coating agent in order to form a coat in the front face of the matter and to raise slipping nature conventionally. If the conventional technique about this silicone coating agent is mentioned, it will be Japanese Patent Publication No. It is indicated by by making 46 No. -3627 official report apply and harden the silicone coating agent which diluted the copolymer of an amino alkyl siloxane and dimethylsiloxane with the organic solvent to metal tabulation sides, such as a razor cutting edge, a subcutaneous needle, scissors, and Metz, that the endurance of surface slipping in metal goods can be improved. Furthermore, it is indicated by by making JP,62-52796,B apply and harden the silicone coating agent which diluted the reactant of an amino-group content silane and an epoxy group content silane, and the resultant with polydyorganosiloxane to the inert solvent on a metal, timber, and a plastics front face that the slipping nature on the front face of spreading may be raised.

[0003] Moreover, the conventional silicone coating agent mentioned above is marketed where a silicone component is diluted with organic solvents, such as toluene, isopropanol, and chlorofluocarbon, to extent 30 to 50% (it is below the same% of the weight), and it adds organic solvents, such as n-hexane, chlorofluocarbon, isopropanol, and chlorinated hydrocarbon, further at the time of an activity, and a silicone component It dilutes so that it may become 2 - 5% extent, and an article is applied and stiffened and a coat is made to form in it.

[0004] However, even if it improved about the silicone component as mentioned above or used it after dilution by the above-mentioned organic solvent, the conventional silicone coating agent has the fault that the slipping nature grant effectiveness on the front face of spreading is not enough, or coat formation of uniform thickness is difficult and tends to produce dryness nonuniformity, a HAJIKI phenomenon, etc., and an improvement of both fault of these was desired.

[0005] Although it is the object which improves this and using the mixed solution of a methylene chloride and a methanol as a dilution solvent is shown in JP,3-292377,A, chlorinated hydrocarbon, such as a methylene chloride, has a possibility of leading to ozone layer depletion like chlorofluocarbon, and an earth ring interface to the activity is not desirable.

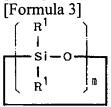
[0006]

[Problem(s) to be Solved by the Invention] This invention is excellent in homogeneity spreading nature, in having been made in view of the above-mentioned situation and excelling in the slipping nature grant effectiveness on the front face of spreading, and it aims at offering the diluent for silicone coating agents which gives a desirable silicone coating agent also from on environmental sanitation further.

[0007]

[Means for Solving the Problem] In order to attain the above-mentioned object, as a result of advancing examination wholeheartedly, when specific low-molecular-weight liquefied silicone is used as a diluent for silicone coating agents, they are excellent in the slipping nature in the front face of the applied article, and this invention persons have uniform thickness, find out that the hardening coat which does not almost have dryness nonuniformity and a HAJIKI phenomenon is obtained, and came to complete this invention.

[0008] That is, the diluent for silicone coating agents of this invention is the general formula-ization 3 [0009].



It is [the cyclosiloxane shown by (as for the inside R1 of a formula a hydrogen atom or a univalent hydrocarbon group is expressed, and m shows the integer of 3-8), and] the general formula-ization 4 [0010].

[Formula 4]
$$R^{1} - Si - O \xrightarrow{R^{1}} Si - O \xrightarrow{R^{1}} Si - R^{1}$$

$$R^{1} - Si - O \xrightarrow{R^{1}} R^{1}$$

it is chosen out of the group which consists of a chain-like siloxane shown by (as for the inside R1 of a formula a hydrogen atom or a univalent hydrocarbon group is expressed, and n shows the integer of 0 or 1-6) one sort -- or -- It is characterized by including two or more sorts of low-molecular-weight siloxanes.

[0011] here -- R1 mutually the same -- or -- difference -- a hydrogen atom -- or -- A univalent hydrocarbon group is expressed, aryl groups, such as alkenyl radicals, such as alkyl groups, such as a methyl group, an ethyl group, and a propyl group, a vinyl group, and an allyl group, a phenyl group, and a tolyl group, are illustrated as a hydrocarbon group, and the ease of carrying out to the hydrogen atom or methyl group of the acquisition of a raw material by the composite ease of carrying out is [among these] desirable.

[0012] Several m of the repeating unit of cyclosiloxane shown by said general formula-ization 3 3-8 It is an integer. The case of nine or more has a slow volatilization rate, and becomes [the clearance after coating coat formation] difficult and is unsuitable. [of a volatilization rate] From a volatilization rate and the composite ease of carrying out, it is m. 3-6 An integer is desirable.

[0013] Moreover, several n of the repeating unit of the chain-like siloxane shown by said general formula-ization 4 0, or 1-6 It is an integer. Like the case of said cyclosiloxane, the case of seven or more has a slow volatilization rate, and becomes [the clearance after coating coat formation] difficult and is unsuitable. [of a volatilization rate] A volatilization rate to n 0 or 1-3 An integer is desirable.

[0014] The silicone active principle of a silicone coating agent the diluent for silicone coating agents of this invention It is used so that it may dilute to 0.1 - 80% of the weight. At less than 0.1 % of the weight, if the coating coat of sufficient thickness becomes is hard to be formed and it exceeds 80 % of the weight, the coating coat of uniform thickness will become is hard to be obtained. it is desirable -- it is used so that it may dilute to 1 - 20% of the weight.

[0015] In addition, although there is especially no limit in the silicone component of a silicone coating agent in this case and various silicone components are usable For example, the copolymer of the amino alkyl siloxane and dimethylsiloxane which were indicated by JP,46-3627,B, The resultant of the reactant

of the amino-group content silane and epoxy group content silane which were indicated by JP 62-52796,B, and polydyorganosiloxane, Japanese Patent Publication No. The constituent which consists of the polyorgano hydrogen siloxane and the nonresponsive organopolysiloxane for the alkenyl radical content polyorganosiloxane indicated by 3 No. -46499 official report, the object for bridge formation, and chain extension is illustrated.

[0016] In these, the copolymer of an amino alkyl siloxane and dimethylsiloxane and the resultant of the reactant of an amino-group content silane and an epoxy group content silane and polydyorganosiloxane are used preferably, and especially the latter resultant is used preferably. As a former example, the following is illustrated concretely.

(1) General formula [0017]

It is polydyorganosiloxane shown by (in X a hydroxyl group or a hydrolysis nature machine, and R2 show a hydrogen atom or a univalent hydrocarbon group, and p shows the integer of 1-10,000 here). The 100 weight sections and (2) General formula [0018]

[Formula 6] Q1 2 N-R3-Si R4 q Y3-q (here -- Q1 -- a hydrogen atom --) A methyl group or -CH2 CH2 NH2, and R3 A divalent hydrocarbon group, R4 a hydrogen atom -- or -- a univalent hydrocarbon group and Y -- a hydroxyl group or a hydrolysis nature machine -- q 0 or 1-2 an integer -- being shown -amino-group content silane shown Silicone coating agent which uses as a principal component the amino-group content polysiloxane obtained by making 1 - 40 weight section react, and carrying out a polymerization.

[0019] It is R2 here. And R4 As a univalent hydrocarbon group, it is R1. The same substituent is illustrated. Moreover, R3 As a divalent hydrocarbon group, -CH2-, -CH2 CH2-, -CH2 CH2-, -CH2 CH2 CH2-, etc. are illustrated. as a hydrolysis nature machine of X and Y, the ORGANO amide groups, such as ORGANO amino-group; N-methyl acetamide radicals, such as ORGANO aminoxy; dimethylamino radicals, such as the ORGANO oxime radicals, such as acyloxy radical; acetone oxime radicals, such as alkenyloxy radical; acetoxy radicals, such as alkoxy group; pro PENOKISHI radicals, such as a methoxy group, an ethoxy radical, and a propoxy group, and a BENZOKISHI radical, and a butanone oxime radical, dimethyl aminoxy, and diethyl aminoxy, a diethylamino radical, and a cyclohexylamino radical, etc. are illustrated. (1) shown by said general formula-ization 5 As polydyorganosiloxane, it is [0020].

[Formula 7]
$$HO \longrightarrow (CH_3)_2 Si O \longrightarrow H$$

$$HO \longrightarrow (C_6 H_5) (CH_3) SiO \longrightarrow H$$
 .

$$HO \leftarrow (C_6 H_5)_2 SiO \rightarrow H$$

$$CH_3 O \longrightarrow (C_6 H_5)_2 Si O \longrightarrow CH_3$$

**** is illustrated. here -- p the integer of 1-10,000 -- it is -- desirable -- It is 5-6,000 and that especially whose viscosity in 25 degrees C is 50-100,000cSt is desirable.

[0021] (2) shown by said general formula-ization 6 As an amino-group content silane gammaaminopropyl triethoxysilane, gamma-aminopropyl methyldiethoxysilane, N-(beta-aminoethyl) aminomethyl trimethoxysilane, gamma-(N-(beta-aminoethyl) amino) propyltrimethoxysilane, gamma-(N-(beta-aminoethyl) amino) propylmethyl dimethoxysilane, N-(beta-aminoethyl) amino MECHIRUTORI butoxysilane, gamma-(N-(beta-(N-(beta-aminoethyl) amino) ethyl) amino)

propyltrimethoxysilane, etc. are illustrated.

[0022] This (2) An amino-group content silane is (1) shown by said general formula-ization 5. Polydyorganosiloxane As opposed to the 100 weight sections A 1-40 weight section activity is carried out. Slipping nature with the good coating coat which will be obtained if fewer than 1 weight section, and the adhesion over a base material become is hard to be acquired, and if [than 40 weight sections] more, good endurance will become is hard to be acquired.

[0023] (1) A polysiloxane and (2) The polymerization reaction with an amino-group content silane mixes both, and if required, it will be obtained by carrying out heating stirring using a catalyst and a solvent. As a catalyst, the catalyst hydrolysis and for condensation reactions, the catalyst for addition reactions, etc. can be suitably chosen according to the class of functional group of a raw material. [0024] Moreover, desired polymerization degree can be acquired by controlling the reaction time of a polymerization reaction, reaction temperature, etc.

[0025] Moreover, as a latter thing, the following is concretely illustrated among the silicone active principles of the desirable silicone coating agent mentioned above.

(3) 1 It is in a molecule. Polydyorganosiloxane which has one silanol group The 100 weight sections and (4) The amino-group content silane and general-formula(b)-izing 8 [0026] which are shown by said (a) general formula-ization 6

[Formula 8] Q2-R5-Si R6 r Z3-r (here -- Q2 -- a glycidoxy radical or an epoxycyclohexyl radical --) R5 A divalent hydrocarbon group and R6 a hydrogen atom -- or -- a univalent hydrocarbon group -- Z -- a hydroxyl group or a hydrolysis nature machine, and r 0 or 1-2 an integer -- being shown -- silicone coating agent which the reactant 0.1 with the epoxy group content silane shown - 20 weight sections are made to react, and uses the resultant as a principal component.

[0027] It is R5 here. As a divalent hydrocarbon group, it is R3. The same radical is illustrated. Moreover, R6 As a univalent hydrocarbon group, it is R1. The same substituent is illustrated. Moreover, the same radical as X is illustrated as a hydrolysis nature machine of Z.

[0028] 1 It is in a molecule. (3) which has a univalent silanol group The polydyorganosiloxane by which the siloxane and piece end which are illustrated by said general formula-ization 5 were blockaded with the silanol group or the hydrolysis nature machine as polydyorganosiloxane, and the other end was blockaded by the trimethylsilyl radical is illustrated. this siloxane -- the viscosity in 25 degrees C -- 20-1,000,000cSt -- desirable -- The thing of 100-100,000cSt is used.

[0029] (a) The thing same as an amino-group content silane as the above-mentioned general-formulaizing 6 is illustrated. Moreover, as an epoxy group content silane shown by said general formula-ization 8 (b), gamma-glycidoxypropyltrimetoxysilane, gamma-glycidoxy propyl methyldimethoxysilane, beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, beta-(3, 4-epoxycyclohexyl) ethyl methyl dimethoxysilane, beta-(3, 4-epoxycyclohexyl) ethyltriethoxysilane, beta-(3, 4-epoxycyclohexyl) ethyl methyldiethoxysilane, etc. are illustrated.

[0030] (4) of an amino-group content silane and an epoxy group content silane a reactant -- amino-group (a) content silane one mol -- receiving -- epoxy group (b) content silane 0.5-3.0 mols -- desirable -- 0.75-1.5 mols are added and it is obtained by making it heat and react under stirring. this (4) Reactant 0.1 - 20 weight section -- desirable -- (3) which contains a silanol group for 1 - 10 weight section Polydyorganosiloxane A silicone coating agent is obtained by mixing with the 100 weight sections, using and heating a solvent and making it react if needed.

[0031] Various kinds of organic solvents can be used for the silicone coating agent shown in this invention in the range which does not spoil the description of this invention. As such an organic solvent, toluene, a xylene, a cyclohexane, Hydrocarbon system solvents, such as n-hexane, n-heptane, naphtha, a mineral spirit, and petroleum benzine, Chloroform, a carbon tetrachloride, a trichloroethylene, perchloroethylene, A halogenated hydrocarbon solvent like 1,1,1-trichloroethane, Ethyl ether, a tetrahydrofuran, an ethers solvent like ethylene glycol diethylether, An alcohols solvent like ketones like ethyl acetate, butyl acetate, an ester solvent like amyl acetate, a methyl ethyl ketone, and methyl isobutyl ketone, a methanol, ethanol, propyl alcohol, and isopropyl alcohol is mentioned.

[Example] An example is given below and this invention is explained concretely. Among an example, the "section" shows the "weight section", "% of the weight" is shown"%" here, and viscosity shows the value in 25 degrees C.

[0033] It is at 80 - 100 ** about the equimolecular amount of 1gamma-aminopropyl trimethoxysilane of examples of preparation, and gamma-glycidoxypropyltrimetoxysilane. Reactant which was made to react for 3 hours and was obtained The 0.5 sections, Viscosity 20,000cSt by which both ends were blockaded by the silanol group The poly dimethylsiloxane 20 section, Viscosity 1500cSt by which the piece end was blockaded by the silanol group and the other end was blockaded by the trimethylsilyl radical It is at 80 degrees C about the mixture which consists of the poly dimethylsiloxane 19.5 section and the toluene 60 section. It was made to react for 8 hours and the transparent and colorless solution (coating agent A) was obtained.

[0034] A silicone active principle silicone coating agent A obtained in examples 1-3, the example 1 of a comparison - the example 1 of 4 preparation using the diluent of the examples 1-3 expressed with a table 1, and the examples 1-4 of a comparison It diluted so that it might become 3%.

[0035] Next, after carrying out flow coating of the above-mentioned diluent to the SUS plate (width-of-face 70mmx die-length 150mm x thickness 0.5mm) which made the front face clarification, desiccation hardening was carried out at the room temperature for 24 hours. In addition, the plate which does not carry out coating was made into the example of reference. While measuring the dynamic friction coefficient of the obtained coating film front face on the following conditions, visual observation of the coating film surface state was carried out, and the following criteria estimated. A result is shown in a table 1.

[0036] Dynamic friction coefficient Measuring condition contact point [-- 25 degrees C, humidity / -- 50%RH.] -- SUS, load -- 80g, rate -- 20 mm/min, temperature

[0037] valuation-basis thickness of a coating film surface state O: -- homogeneity and O: -- almost -- homogeneity and **: -- a little -- those with nonuniformity, and x:ununiformity.
[0038]

[A table 1]

例	希釈剤	動摩擦係数	表面状態
実施例1	ヘキサメチルジシロキサン	0.114	0
実施例2	オクタメチルシクロテトラシロキサン	0.118	0
実施例3	デカメチルシクロペンタシロキサン	0. 120	0
比較例1 比較例2	□へキサン フロン113	0. 150 0. 123	Δ ©
比較例3	塩化メチレン	0. 125	Ō
比較例4	トルエン	*	×
参考例	(コーティング無し)	0. 365	_

*:膜が不均一で、測定値のばらつきが大きく、正確な数値を測定できない。

[0039]

[Effect of the Invention] The diluent for silicone coating agents of this invention is excellent in slipping nature, and its thickness is uniform and it gives the silicone coating agent which can form the hardening coat which does not almost have dryness nonuniformity and a HAJIKI phenomenon. The diluent for silicone coating agents of this invention has still less effect to earth environment. Therefore, if silicone coating is carried out using the diluent of this invention, the full realization at the time of **** of a

metal hypodermic needle can be decreased substantially, for example. Moreover, about a cutter, Metz, and scissors, the resistance at the time of a cut is reduced and effectiveness, such as going out well by the light force, is given.

[0040] The diluents for silicone coating agents of this invention are coats for an improvement, such as slipping nature, such as the fork of tableware, a needlework needle, a zipper, a stapler needle, a comb, a card, a ticket, and coin, and a thing further used for a bottle coat, a plastics coat, a timber coat, etc. preferably including coats, such as an above-mentioned hypodermic needle, a cutter, Metz, scissors, a razor, and a knife.

[Translation done.]